

**In-situ micro-FTIR study of thermal changes of organics in Tagish Lake meteorite
– Behavior of aliphatic oxygenated functions and effects of minerals –**

Yoko Kebukawa,^{1*} Satoru Nakashima,¹ Keiko Nakamura-Messenger,² and Michael E. Zolensky²

¹Department of Earth and Space Science, Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560-0043, Japan.

²Astromaterials Research and Exploration Science, KT, NASA Johnson Space Center, Houston, TX 77058, USA.

* Corresponding author: yoko.soleil@ess.sci.osaka-u.ac.jp

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Abstract

Systematic in-situ FTIR heating experiments of Tagish Lake meteorite grains have been performed in order to study thermal stability of chondritic organics. Some aliphatic model organic substances have also been used to elucidate effects of hydrous phyllosilicate minerals on the thermal stability of organics. The experimental results indicated that organic matter in the Tagish Lake meteorite might contain oxygenated aliphatic hydrocarbons which are thermally stable carbonyls such as ester and/or C=O in ring compounds. The presence of hydrous phyllosilicate minerals has a pronounced effect on the increase of the thermal stability of aliphatic and oxygenated functions.

These oxygenated aliphatic organics in Tagish Lake can be formed during the aqueous alteration in the parent body and the formation temperature condition might be less than 200°C, based especially on the thermal stability of C–O components. The hydrous phyllosilicates might provide sites for organic globule formation and protected some organic decomposition.

INTRODUCTION

Chondritic organic matter preserves signatures of various evolutionary steps from presolar materials, through aqueous alteration in the parent asteroid body up to delivery to the Earth (Botta and Bada 2002; Ehrenfreund et al. 2002; Sephton 2002; Nakamura et al. 2002; Cody and Alexander 2005; Nakamura-Messenger et al. 2006). Furthermore, the organic components are possible raw materials for the chemical evolution toward life (Cronin 1998; Botta and Bada 2002; Ehrenfreund et al. 2002; Sephton 2002).

The Tagish Lake meteorite fell on 18 January 2000, on the frozen surface of the Taku Arm branch of Tagish Lake, Canada (Brown et al. 2000; Hildebrand et al. 2006). It is a new type carbonaceous chondrite possibly from a primitive organic-rich (D/P-type) asteroid (Hiroi et al. 2001). The matrix of Tagish Lake meteorite consists mainly of Mg-rich phyllosilicates including smectite and serpentine, Mg-Fe carbonates, Fe-Ni sulfides and magnetite (Zolensky et al., 2002; Nakamura et al. 2003a). There are two dominant lithologies in the meteorite, one containing significantly more carbonate than the other. The total carbon content is 5.4 wt.% while the organic carbon content is 1.7 wt.% (Brown et al. 2000). HF/HCl digestion of Tagish Lake meteorite yielded approximately 2.4 % of its total weight as a carbonaceous residue, with the general formula $C_{100}H_{46}N_{10}O_{15}$ accounting for over 99% of the total organic carbon (Pizzarello et al. 2001). The bulk oxygen isotopic composition of Tagish Lake suggests an aqueous alteration temperature of approximately 0°C (Clayton and Mayeda 2001) or lower than 80°C (Baker et al. 2002), depending upon the interpretation of the data. The presence of poorly-graphitized organic material in the carbonate-poor lithology could indicate temperatures lower than 100 °C (Zolensky *et al.* 2002).

Insoluble organic matter (IOM) in carbonaceous chondrites, which is insoluble with HCl/HF treatment, has been partially characterized over recent decades (Botta and Bada

2002; Sephton 2002; Ehrenfreund et al 2002, and references there in). IOM is often described as ‘condensed aromatic cores, connected by aliphatic and ether linkages and with various functional groups attached’ (Sephton 2002).

Fourier transform infrared (FTIR) spectroscopy is a non-destructive technique for whole organic components, and has been previously successfully applied to chondritic organic matter (Hayatsu et al. 1977; Ehrenfreund et al. 1991, 1992; Salisbury et al. 1991; Murae 1994). FTIR studies of the Tagish Lake meteorite (Flynn et al., 2001; Keller and Flynn, 2001; Nakamura et al., 2002, 2003b; Matrajt et al., 2004) report absorption bands due to organic functional groups such as aliphatic C–H, C=O, C–O together with structural O–H of phyllosilicate minerals, carbonate and Si–O bonds. Nakamura et al. (2002) and Nakamura-Messenger et al. (2006) indicated that organic globules of several hundreds of nm in size are disseminated among phyllosilicates, suggesting interactions between organics and these minerals. Nakamura et al. (2003b) conducted preliminary in-situ FTIR heating experiments of organic matter of the Tagish Lake meteorite and indicated varying thermal stabilities of different organic functional groups.

In this study, systematic in-situ FTIR heating experiments of the Tagish Lake meteorite have been performed in order to explore organic-inorganic interactions. Both IOM and soluble organic fractions can be studied with this method without acid treatments. Some aliphatic model organic substances have also been used to elucidate the effects of phyllosilicate minerals on the thermal transformation of organic functional groups. Based on the heating behavior of chondritic organic matter, possible evolution pathways of organic material in the D/P type asteroids are discussed.

SAMPLES AND EXPERIMENTAL TECHNIQUES

Tagish Lake Meteorite Sample

We selected what we believed to be principally carbonate-poor lithology from sample of pristine (i.e. recovered frozen) Tagish Lake, recognizing that it is impossible to establish this definitively without first making thin sections, which would have seriously compromised the organic material (Zolensky *et al.* 2002).

For the present in-situ FTIR experiments, sample powders (approximately 100 μm) were pressed between two aluminum disks (0.08 mm thick) using an oil pressure pump at about 100 kgw/cm^2 to make the sample flat. The two Al disks were then separated and the resultant flattened grain on an Al disk was used for IR spectroscopy.

Terrestrial organic contamination has been suggested by several authors for the carbonaceous chondrites (e.g. Botta and Bada 2002). They pointed out that aliphatic hydrocarbons can be contributed by terrestrial biological and petroleum products. However, our Tagish Lake samples were from carefully-extracted interior chips of the pristine (recovered frozen) fall material, and terrestrial contamination should have been minor. After thawing in N_2 , the samples were kept in a N_2 -purged desiccator in a clean room at a temperature of approximately 23°C, so degradation, including oxidation, were absolutely minimized.

Model Substances

We prepared or obtained the following model standard compounds in order to compare thermal changes of organic functions in the presence of minerals with those of the chondritic organic matter.

- (1) *n*-Octadecane $\text{CH}_3(\text{CH}_2)_{16}\text{CH}_3$, Kanto Chemical Co., Inc., Lot No. 203D2382.
- (2) Stearic acid $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$, Wako Pure Chemical Industries, Ltd. 193-04045, Lot No. CAN1225.
- (3) Antigorite natural sample (fine grained, grain size of several tens of

micrometers or less) $(\text{Mg, Fe}^{2+})_3\text{Si}_2\text{O}_5(\text{OH})_4$, monoclinic, Nihon Chikagakusha, No. #14-4-12-1 from Nakanochaya, Miyatsu, Kyoto, Japan.

Stearic acid was selected to represent C=O functions attached to aliphatic chains of chondritic organic matter. Octadecane is a saturated aliphatic chain with 18 carbons without the carboxyl. These compounds had the advantage of being solids at room temperature (Octadecane melting point is 27-28°C, (Baumann et al. 1966), stearic acid: 69.3°C (Zhu et al. 2005)). Antigorite was chosen to represent Mg-rich serpentine minerals, which are one of the major Tagish Lake matrix minerals. In order to study the effects from the presence of other phyllosilicate minerals further studies will be required.

Octadecane and stearic acid were diluted to about 1 wt.% with KBr powder using an alumina mortar and pestle. They were also mixed with antigorite to obtain a mixture with 1 to 10% organic substances in the antigorite matrix.

IR Microspectroscopy

A ceramic infrared light source, a Mercury-Cadmium-Telluride (MCT) detector and a $\times 16$ Cassegrain mirror were used in the microscopic Micro-FTIR (JASCO FT-IR-620+IRT30). The background spectra were collected on an identical Al disk at room temperature.

Transmission-reflection spectra in the range 4000-1000 cm^{-1} were collected at room temperature on the Tagish Lake grains on Al disks, with a $100 \times 100 \mu\text{m}^2$ aperture. Infrared incident light was first transmitted through the sample, which was typically a few tens of micrometers thick, then reflected on the surface of Al disk, and again transmitted through the sample.

Step Heating Experiments

For in-situ heating measurements, sample grains on Al disks were set onto a heating stage (LINKAM FTIR 600) and placed into the micro-FTIR. After measuring the sample spectra at room temperature, the samples were heated at 10°C/min from room temperature to 500°C using the heating stage. During the heating, sample spectra were collected from the same location at every 10°C.

Some IR absorption bands were analyzed quantitatively to track decreases of the components in the Tagish Lake meteorite (Fig. 1). The following peak heights were determined with corresponding baselines (Table 1):

- (1) 2965, 2935, 2875 cm^{-1} peaks with 3020-2820 cm^{-1} baseline.
- (2) 1780 cm^{-1} peak with 1820-1750 cm^{-1} baseline.
- (3) 1265 cm^{-1} peak with 1283-1250 cm^{-1} baseline.

Peak height errors in absorbance of aliphatic C–H stretching (2965, 2935, 2875 cm^{-1}), C=O stretching (1780 cm^{-1}) and C–O stretching (1265 cm^{-1}) were ± 0.0008 , ± 0.01 and ± 0.0009 respectively, at the maximum. Therefore, errors associated with the data in the figures are generally included in the symbol sizes.

IR spectra for the model substances are shown in Fig. 2. Table 1 shows analyzed peak positions with corresponding baselines for aliphatic C–H stretching (approximately 2955, 2925 cm^{-1} : error ± 0.001) and C=O stretching (approximately 1710 cm^{-1} : ± 0.03). C=O peak heights have relatively high errors due to the absorption bands of atmospheric moisture water around 1640 cm^{-1} .

RESULTS

IR Spectra at Room Temperature

Fig. 1 shows micro-FTIR absorption spectra of an unheated Tagish Lake grain. The IR spectra show a sharp absorption feature at 3685 cm^{-1} due to structural hydroxyl (O–H). A broad O–H stretching band around 3450 cm^{-1} and an H–O–H bending band

around 1640 cm^{-1} are probably due to water molecules loosely adsorbed to minerals (Murae 1994) and as interlayer molecular water in phyllosilicates (Keller and Flynn 2001; Quirico and Bonal 2004). Serpentine and saponite are reported in the matrix of Tagish Lake (Zolensky et al. 2002; Nakamura et al. 2003a), and 3685 and 3450 cm^{-1} bands correspond to these minerals.

IR spectra for Tagish Lake show three absorption features representing aliphatic C–H stretching at 2965 , 2935 , 2875 cm^{-1} . The 2965 and 2875 cm^{-1} peaks are due to asymmetric and symmetric stretching absorptions of CH_3 , respectively. The 2935 cm^{-1} peak is due to CH_2 groups. Absorption features at 1780 cm^{-1} and 1265 cm^{-1} can be due to C=O stretching and C–O stretching vibrations, respectively. These C=O and C–O bands suggest the presence of O–C=O (ester) components (Nakamura et al. 2002; Vollhardt and Schore 2007). A broad band between 1465 – 1410 cm^{-1} can be due to aliphatic C–H bending and possibly some carbonate. A strong band around 1100 cm^{-1} is from Si–O stretching absorption within silicates. The band around 2350 cm^{-1} is caused by atmospheric CO_2 .

Fig. 2a-e show micro-FTIR absorption spectra for octadecane, stearic acid, antigorite, octadecane + antigorite and stearic acid + antigorite, respectively. Almost all of these spectra have a broad O–H stretching absorption around 3450 cm^{-1} and an H–O–H bending band around 1635 cm^{-1} due to water molecules adsorbed to KBr or antigorite. Three peaks of aliphatic C–H stretching absorption at 2955 , 2925 – 2915 , 2855 – 2850 cm^{-1} and C–H bending at 1470 cm^{-1} are observed in all of the spectra except antigorite. The 2955 cm^{-1} peak is due to CH_3 stretching absorption and the 2925 – 2915 and 2855 – 2850 cm^{-1} peaks are due to CH_2 . Spectra for stearic acid with or without antigorite show features at 1700 cm^{-1} due to C=O stretching absorption of carboxyl. The spectra for antigorite, octadecane + antigorite and stearic acid + antigorite show bands due to antigorite: a sharp peak at 3680 – 3670 cm^{-1} and smaller feature at 3570 – 3560 cm^{-1} representing structural O–H and strong bands 1200 , 1180 cm^{-1} and around 1100 cm^{-1}

due to Si–O stretching absorption bands.

Step Heating Experiments

Tagish Lake Meteorite

Spectra from the Tagish Lake meteorite at 26, 100, 200, 300, 400 and 500°C during step heating experiments are shown in Fig. 3. Changes in some peak heights during heating are presented in Figs. 4 and 5.

During step heating, the aliphatic C–H absorption features at 2965, 2935, 2875 cm^{-1} initially increased up to 80°C, then decreased rapidly from 110 to 300°C, and finally disappeared at 310–320°C (Fig. 4a). The peak height ratio 2965/2935 cm^{-1} (CH_3/CH_2 ratio) for the Tagish Lake meteorite initially decreased from 1.6 to 1.3 from 50°C to 200°C. The CH_3/CH_2 ratio then rapidly increased to 2.6 (with large errors) with further heating (up to 290°C) (Fig. 4b). The changes in CH_3/CH_2 ratio might reflect some reaction mechanisms such as oxidation and catalytic cracking.

The peak height of the 1780 cm^{-1} feature (C=O) of Tagish Lake did not show significant changes until 250°C. However, above 250°C, the 1780 cm^{-1} peak decreased, persisting until 500°C (Fig. 5a). The 1265 cm^{-1} peak (C–O) decreased gradually from 25°C up to approximately 200°C (Fig. 5b).

Model Substances

The peak heights for aliphatic C–H (CH_3 : 2958–2954 cm^{-1} , CH_2 : 2927–2915 cm^{-1}) of octadecane decreased rapidly during heating to 80°C, then decreased slightly up to 500°C (Fig. 6a). The C–H absorption features (CH_3 : 2955–2954 cm^{-1} , CH_2 : 2927–2917 cm^{-1}) of stearic acid decreased first during heating to approximately 60°C, then increased up to 100°C. Above that temperature, they decreased rapidly to 160°C (Fig. 7a). The C=O absorption feature (1715–1700 cm^{-1}) of stearic acid showed almost the same behavior as the CHs (Fig. 7a).

The peak heights for aliphatic C–H (CH_3 : 2957 cm^{-1} , CH_2 : 2926 cm^{-1}) of octadecane heated with antigorite increased slightly up to 60°C and then rapidly decreased until 130°C . The CH_3 peak increased slightly from 130°C to 500°C , while the CH_2 peak remained essentially unchanged (Fig. 6b). However, these peaks were influenced by the changes in O–H bands of antigorite.

The C–H absorption bands (CH_3 : 2954 cm^{-1} , CH_2 : $2933\text{--}2919\text{ cm}^{-1}$) of stearic acid heated with antigorite increased at first to 60°C , then decreased rapidly between $60\text{--}70^\circ\text{C}$, then increased again to around 130°C . Between $130\text{--}170^\circ\text{C}$ the CH_2 peak height increased while the CH_3 peak height decreased. After 170°C , the both C–H peaks decreased to become almost zero around 350°C (Fig. 7b). The C=O absorption feature ($1714\text{--}1700\text{ cm}^{-1}$) of stearic acid + antigorite decreased during heating to 190°C (Fig. 7b). Thus, the C–H peaks of both octadecane and stearic acid in the presence of antigorite persisted to significantly higher temperatures than those heated without antigorite.

The peak height ratio CH_3/CH_2 (approximately $2955/2925\text{ cm}^{-1}$) for octadecane decreased from 0.6 to 0.3 up to around 80°C then increased gradually to 0.9 (Fig. 8a). The CH_3/CH_2 ratio for octadecane + antigorite decreased from 0.5 to 0.3 from 70 to 100°C and then increased rapidly to 0.9 (Fig. 8b). The CH_3/CH_2 ratio for stearic acid did not show significant changes, remaining at approximately 0.3 during heating (Fig. 9a). On the other hand, this ratio for stearic acid + antigorite decreased from 0.6 to 0.4 from 130 to 210°C , and finally increased to 0.9 (Fig. 9b).

DISCUSSION

IR Signatures of the Tagish Lake Meteorite and Model Compounds

The IR absorption spectra for unheated Tagish Lake meteorite show a sharp peak at 3685 cm^{-1} due to structural O–H and a strong peak at 1100 cm^{-1} due to Si–O (Fig. 1),

due principally to the presence of the hydrous phyllosilicates serpentine and saponite (Zolensky et al. 2002).

Saponite $((M^+)_{0.45}(Mg_{2.91}Fe^{3+}_{0.16}Al_{0.03})(Si_{3.58}Al_{0.42})O_{10}(OH)_2)$ should have an O–H peak at 3650-3640 cm^{-1} and an Si–O peak at 1010-1000 cm^{-1} (Kodama 1985). However, Tagish Lake does not show clear bands at 3650-3640 cm^{-1} and 1010-1000 cm^{-1} , which is expected because serpentine, rather than saponite, is the principal phyllosilicate mineral in Tagish Lake (Zolensky et al. 2002).

The representative serpentine mineral antigorite shows a strong O–H peak at 3680-3670 cm^{-1} and a smaller one at 3570-3560 cm^{-1} . Its Si–O absorption band is at around 1100 cm^{-1} with smaller bands at 1200 and 1180 cm^{-1} . The O–H peak position for phyllosilicates is known to depend on the nature of adjacent metal ions, and the frequency of Mg O–H vibration is higher than that of Fe O–H (Martinez-Alonso et al. 2002). The chemical composition of our antigorite sample was Mg rich (41.1 wt. % MgO and 1.7 wt. % FeO: Uehara and Shirozu 1985). Therefore, the peak position at 3685 cm^{-1} for the Tagish Lake meteorite should correspond to Mg-rich serpentine. The phyllosilicates in Tagish Lake meteorite are indeed reported to be Mg-rich (16.97-32.18 wt. % MgO and 10.72-27.14 wt. % FeO: Zolensky et al. 2002).

Aliphatic C–H peaks of the Tagish Lake meteorite (2965, 2935 and 2875 cm^{-1}) are situated at higher frequencies than the model organic matter (2955, 2915 and 2850 cm^{-1} for octadecane; 2955, 2915 and 2850 cm^{-1} for stearic acid) (Fig. 1, 2). It is not likely to reflect the difference of aliphatic chain length, since the changes in length of aliphatic chains from C_{18} to C_{40} do not yield the peak shifts significantly (about 1-3 cm^{-1} to the higher frequency). Oxygenated C–H bonds are reported to show absorptions at higher frequencies, such as in diethyl ketone ($C_2H_5C=OC_2H_5$: 2977, 2936 and 2883 cm^{-1}) (Bellamy 1958). Therefore, aliphatic compounds in the Tagish Lake meteorite might include some oxygenated functions.

The aromatic moieties in the IOM of the Tagish Lake meteorite are reported to be

highly substituted (Cody and Alexander 2005). Although Pizzarello et al. (2001) suggested that graphitic carbons are dominant over aliphatic hydrocarbon, aromatic C–H absorption around 3050 cm^{-1} was not observed. This can be due to the highly substituted nature of aromatics.

The Tagish Lake meteorite has a C=O peak at 1780 cm^{-1} and C–O at 1265 cm^{-1} , while stearic acid has C=O peak at 1700 cm^{-1} without a C–O peak. Therefore, the main oxygenated functions in Tagish Lake may not be carboxyls (COOH). The presence of C=O and C–O peaks was previously attributed to O–C=O (ester) components in Tagish Lake (Nakamura et al., 2002). The peak positions for ester compounds (R_1COOR_2) are generally at $1750\text{--}1735\text{ cm}^{-1}$ (Vollhardt and Schore 2007). However, $\text{R}_1\text{COOCOR}_2$ type compounds have bands at $1790\text{--}1740\text{ cm}^{-1}$ and $1850\text{--}1800\text{ cm}^{-1}$. Indeed, Tagish Lake has a weak band at 1840 cm^{-1} in addition to the 1780 cm^{-1} band. The peak positions of oxygenated functions in ring compounds are reported to be at higher frequencies, such as in cyclobutanone at 1780 cm^{-1} (Vollhardt and Schore 2007). Therefore, C=O components in Tagish Lake could be due to ester compounds and/or ketone in ring compounds.

These results seem to be consistent with NMR studies of chondritic insoluble organic matter (IOM) by Cody and Alexander (2005). They suggested that the Tagish Lake meteorite IOM has COOR (i.e., carboxyl, where $\text{R} = \text{H}$ and/or C) and C=O (e.g., ketone). Our results suggest that the majority of COOR seems to be ester (COOC) rather than carboxyl (COOH).

Heating Behavior of Tagish Lake Meteorite and Model Compounds

Heating Behavior of Long Chain Aliphatic Hydrocarbons (Octadecane)

In order to compare the thermal behavior of Tagish Lake organic matters with some model compounds, octadecane was first studied as a representative long chain saturated aliphatic hydrocarbon. The results of step heating experiments of octadecane showed

that this compound persisted only to 80°C without antigorite and to about 130°C in the presence of antigorite (Fig. 6). This instability of octadecane is quite different from the measured persistence of aliphatic CHs to 300°C in Tagish Lake (Fig. 4a). The significant decrease and increase in CH₃/CH₂ ratio for octadecane during the heating are considered to reflect oxidation and thermal cracking processes in the presence of antigorite based on organic catalysis studies (Eisma and Jurg 1969; Potatuyev et al. 1971; Vollhardt and Schore 2007) (Fig. 8b). The changes in the CH₃/CH₂ ratio for Tagish Lake show different trends to that of octadecane, suggesting again rather different thermal changes for aliphatic compounds in Tagish Lake. Therefore, aliphatic compounds in Tagish Lake are not considered to be long chain saturated aliphatic compounds.

Heating Behavior of Carboxylated Long Chain Oxygenated Aliphatic Compounds (Stearic Acid)

Stearic acid was used to represent a long chain saturated aliphatic hydrocarbon with an end carboxyl. The results of step heating experiments of stearic acid showed that this compound persisted to about 160°C without antigorite and to about 350°C in the presence of antigorite (Fig. 7). This persistence of stearic acid in the presence of antigorite is not far from that of aliphatic CHs to 300°C in Tagish Lake (Fig. 4a). The changes in the CH₃/CH₂ ratio for Tagish Lake (Fig. 4b) show somewhat similar changes as these for stearic acid during heating. Therefore, aliphatic compounds in Tagish Lake are closer to oxygenated saturated aliphatic compounds. The thermal persistence of aliphatic compounds with antigorite might be possibly due to an interaction of these components with the phyllosilicates' surfaces.

Heating Behavior of C=O in Stearic Acid

C=O bonds in stearic acid showed faster decrease with heating up to 190°C, even

with antigorite (Fig. 7). This instability of C=O in carboxyls is quite different from the persistence of C=O up to 500°C in Tagish Lake. The decrease in C=O in stearic acid can be explained by the decarboxylation process producing CO₂ based on a hydrothermal decarboxylation of acetic acid (Belsky et al. 1999). As is discussed above, C=O bonds in Tagish Lake are considered to be mainly ester and/or C=O in ring compounds. These carbonyl C=O compounds may not easily lose CO₂ and cannot be decarboxylated.

Although the mechanisms of thermal behavior of these model compounds remain to be explored in detail, their comparison with those for Tagish Lake suggests that organic matter in there might contain oxygenated aliphatic compounds and that the main oxygenated functions can be thermally stable carbonyls such as ester and/or C=O in ring compounds. It should be noted that the presence of hydrous phyllosilicate minerals such as antigorite has a pronounced effect in increasing the thermal stabilities of aliphatic compounds.

Implication to the Organic Evolution in Astro-Materials

Based on the above results on heating behavior of organic matter in the primitive carbonaceous chondrite of Tagish Lake, the following organic evolution can be considered. Simple low-molecular weight organic compounds and polycyclic aromatic hydrocarbons (PAHs) were contained in dust particles together with ice and silicate minerals (Greenberg 1998; Rietmeijer 2002; Nakamura-Messenger et al. 2006). These particles were accreted into asteroids and the interior temperature increased well above 0°C by the heat generated from radioactive decay of short-lived isotopes such as ²⁶Al (McSween 1999).

Melting of ices occurred and wet aqueous conditions were present in the asteroids. Although details of aqueous organic evolutions remain to be studied by further systematic wet experiments, some oxygenated aliphatic compounds can be formed

during this aqueous alteration. Ester R_1COOR_2 compounds can be formed by dehydration-condensation from R_1OH and R_2COOH . In fact, some hydroxyl and carboxyl compounds were reported in carbonaceous chondrites (Cody et al. 2002; Cody and Alexander 2005; Remusat et al. 2005). These ester compounds might have had a membrane-like character and formed the organic globules in the Tagish Lake meteorite (Nakamura et al. 2002). Our preliminary hydrothermal simulation experiments indicate that organic globules can be formed on rock surfaces at temperatures around 100 °C from a threonine solution (amino acid having both OH and COOH) around pH=7 (Iwamoto et al. 2006). Matrix mineral surfaces might have provided sites for organic globule formation. In addition to these ester-like globules, some other complex oxygenated compounds such as C=O in ring compounds could have formed.

From the thermal behavior of organic functional groups studied here, the C–O components were the least stable functions, decreasing in abundance from about 60°C, mostly disappearing by 200°C (Fig. 5b). Since this component could be a part of the ester-like compounds forming globules, the temperature condition of aqueous alteration process might be less than about 200°C.

Since the presence of antigorite increased the thermal stability of model organic compounds such as aliphatic and carboxylic functions, the presence of hydrous phyllosilicate minerals should have served to protect some organic compounds, especially oxygenated functions which were otherwise thermally unstable.

CONCLUSIONS

IR microspectroscopy of the Tagish Lake meteorite grains was performed in order to study the nature of organic components. The IR spectra show a sharp peak at 3685 cm^{-1} due to structural O–H associated with Mg-rich serpentine. Aliphatic C–H stretching absorptions at 2965, 2875 cm^{-1} due to CH_3 and 2935 cm^{-1} due to CH_2 groups were recognizable. The presence of 1780 cm^{-1} (C=O) and 1265 cm^{-1} (C–O) bands

suggest the presence of O–C=O (ester) components. The C=O band can also be from C=O in ring compounds.

In-situ IR heating experiments of the Tagish Lake meteorite and model substances (octadecane and stearic acid, and those with antigorite) were conducted to compare thermal behavior of C–H, C=O and C–O absorption peaks.

The saturated long chain aliphatic hydrocarbons (octadecane) were found to be lost during heating to 80°C without antigorite and until about 130°C in the presence of antigorite. On the other hand, stearic acid persisted to about 160°C without antigorite and to about 350°C with antigorite. This persistence of stearic acid in the presence of antigorite is similar to that of aliphatic CHs to 300 °C in the Tagish Lake meteorite.

The significant decrease and increase in CH₃/CH₂ ratio for octadecane during heating are considered to reflect oxidation and thermal cracking processes in the presence of antigorite. The changes in CH₃/CH₂ ratio for Tagish Lake show different trends to that of octadecane but are close to those for stearic acid during the heating experiments. Therefore, aliphatic compounds in Tagish Lake are similar to oxygenated saturated aliphatic compounds. And these aliphatic compounds persist to higher temperatures in the presence of antigorite, possibly due to interaction of these components with the surfaces of phyllosilicates.

The persistence of C=O bonds up to 500°C in Tagish Lake is quite different from their behavior in stearic acid, where they were lost during heating to 190°C even in the presence of antigorite, possibly due to decarboxylation producing CO₂. C=O bonds in Tagish Lake are considered to be mainly ester and/or C=O in ring compounds, which cannot be easily decarboxylated.

The organics in Tagish Lake might contain oxygenated aliphatics and the main oxygenated functions can be thermally stable carbonyls such as ester and/or C=O in ring compounds. The presence of hydrous phyllosilicate minerals has a pronounced effect in increasing the thermal stabilities of aliphatic compounds. The results of the heating

experiments we performed suggest that the presence of hydrous phyllosilicates should have helped to prevent evaporation and catalyze oxidation and/or thermal cracking of chondritic organic matter in heated asteroids.

All these results suggest that the oxygenated aliphatic organics in Tagish Lake might have been formed during the aqueous alteration in the parent asteroid and that the formation temperature should have been less than about 200°C, based especially on the thermal stability of C–O components. The hydrous phyllosilicates may have provided sites for organic globule formation and prevented some organic decomposition.

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Table 1. Peak positions (cm^{-1}) with corresponding baselines used for determining the peak heights for model compounds and organic matter of Tagish Lake.

	Peak position [baselines]							
	C-H CH ₃	CH ₂	CH ₃	C=O			C-O	
Tagish Lake	2965	2935	2875	[3020-2820]	1780	[1820-1750]	1265	[1283-1250]
Octadecane	2958-2954	2927-2915	—	[3050-2800]	—		—	
Octadecane	2957	2926	—	[3120-2770]	—		—	
+ antigorite								
Stearic acid	2955-2954	2927-2917	—	[3000-2800]	1715-1700	[1830-1370]	—	
Stearic acid	2954	2933-2919	—	[3120-2770]	1714-1700	[1900-1500]	—	
+ antigorite								

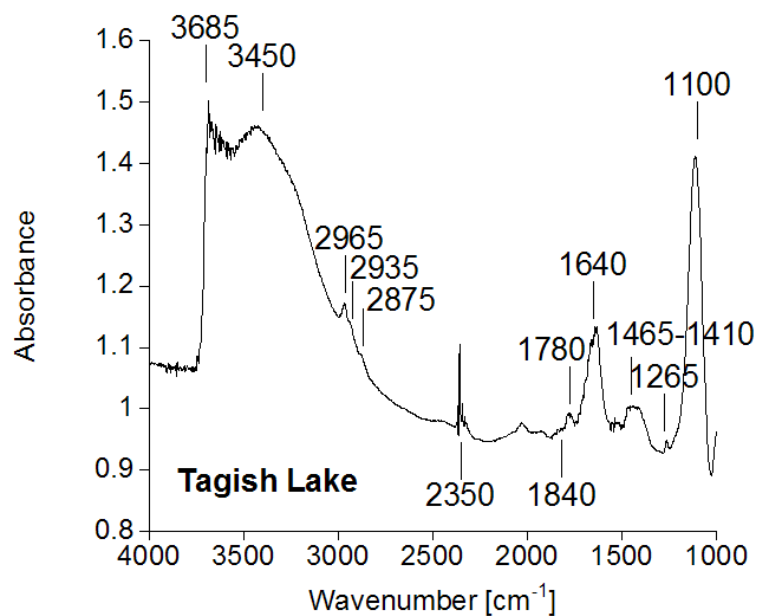


Fig. 1. Infrared absorption spectra of unheated Tagish Lake meteorite. 3685 cm^{-1} : structural O–H; 3450 cm^{-1} : O–H stretching of water; 2965, 2935, 2875 cm^{-1} : aliphatic C–H stretching; 1780 cm^{-1} : C=O stretching of organics; 1640 cm^{-1} : H–O–H bending; 1465–1410 cm^{-1} : aliphatic C–H bending + carbonates; 1265 cm^{-1} : C–O stretching of organics; 1100 cm^{-1} : Si–O stretching of silicates.

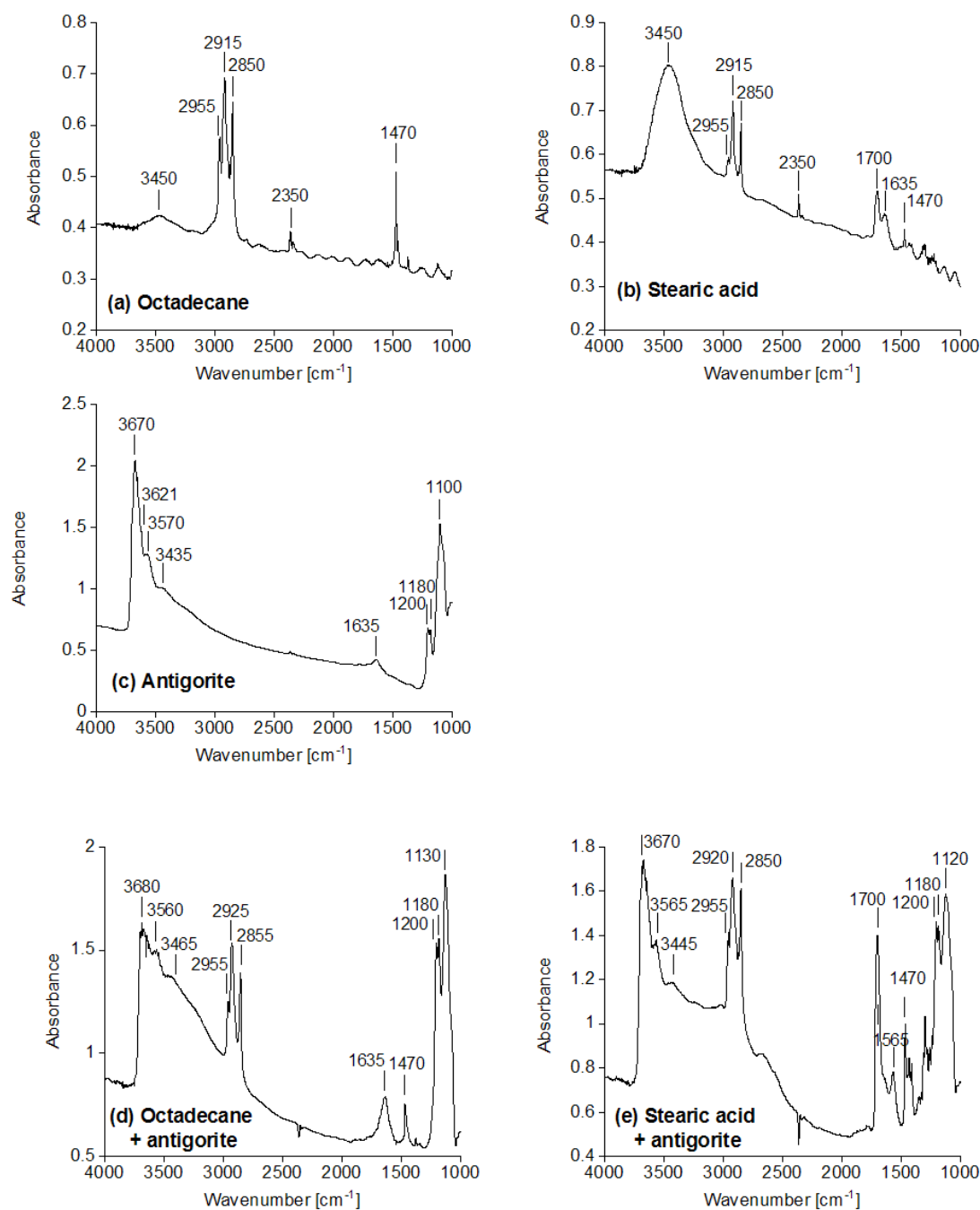


Fig. 2. Infrared absorption spectra of (a) octadecane, (b) stearic acid, (c) antigorite, (d) octadecane + antigorite and (e) stearic acid + antigorite. 3680-3670, 3570-3560 cm^{-1} : structural O-H; 3450 cm^{-1} : O-H stretching of water; 2955, 2925-15, 2855-2850 cm^{-1} : aliphatic C-H stretching; 1700 cm^{-1} : C=O stretching of carboxyl; 1635 cm^{-1} : H-O-H bending of water; 1470 cm^{-1} : aliphatic C-H bending; 1200, 1180 cm^{-1} , around 1100

cm^{-1} : Si–O stretching.

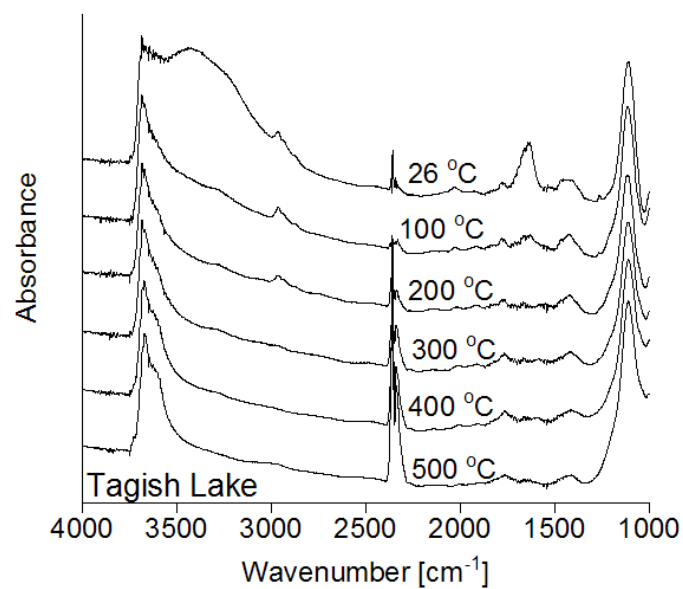


Fig. 3. Infrared absorption Spectra of Tagish Lake meteorite at 26, 100, 200, 300, 400 and 500 °C during the step heating experiments.

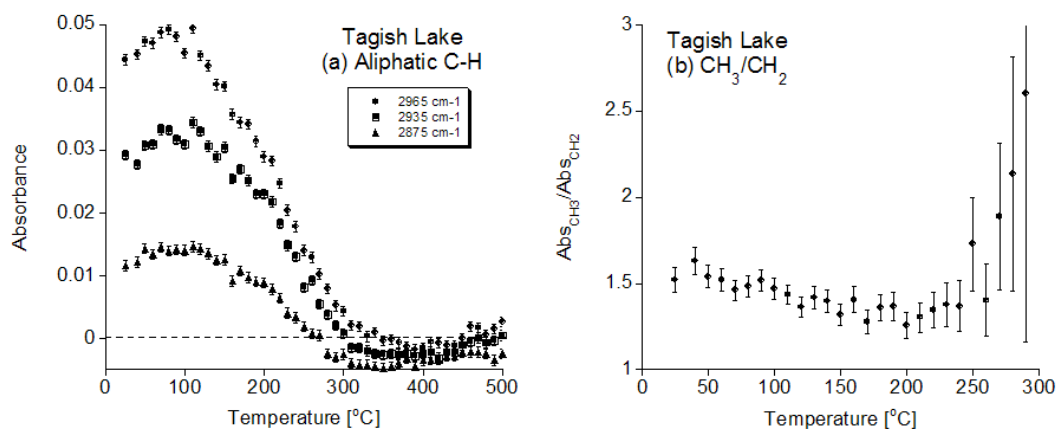


Fig. 4. Changes with temperature of (a) aliphatic C–H peaks at 2965, 2935, 2875 cm^{-1} with 3020–2820 cm^{-1} baseline and (b) peak height ratio CH_3/CH_2 (2965/2935 cm^{-1}) for Tagish Lake meteorite.

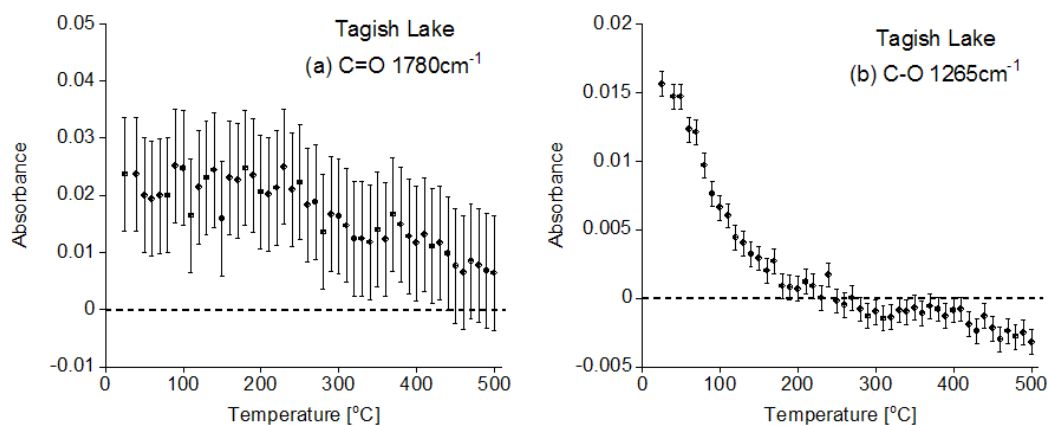


Fig. 5. Changes with temperature of (a) C=O peak height at 1780 cm^{-1} with 1820–1750 cm^{-1} baseline and (b) C–O peak height at 1265 cm^{-1} with 1283–1250 cm^{-1} baseline for Tagish Lake meteorite.

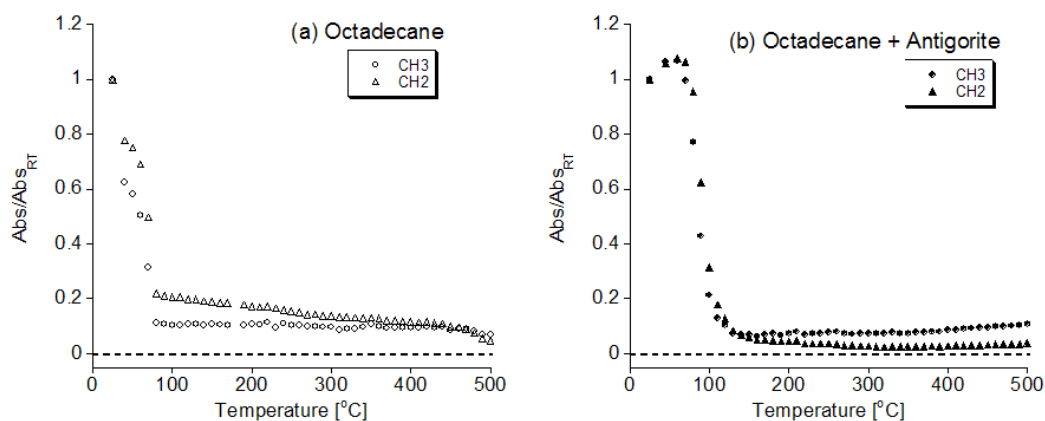


Fig. 6. Changes with temperature of the peak heights for aliphatic C–H of (a) octadecane, 2958-2954 cm^{-1} and 2927-2915 cm^{-1} peaks with 3050-2800 cm^{-1} baseline and (b) octadecane with antigorite, 2957 cm^{-1} and 2926 cm^{-1} peaks with 3120-2770 cm^{-1} baseline. The peak heights (absorbance: Abs) are normalized to their values at room temperature (Abs_{RT}).

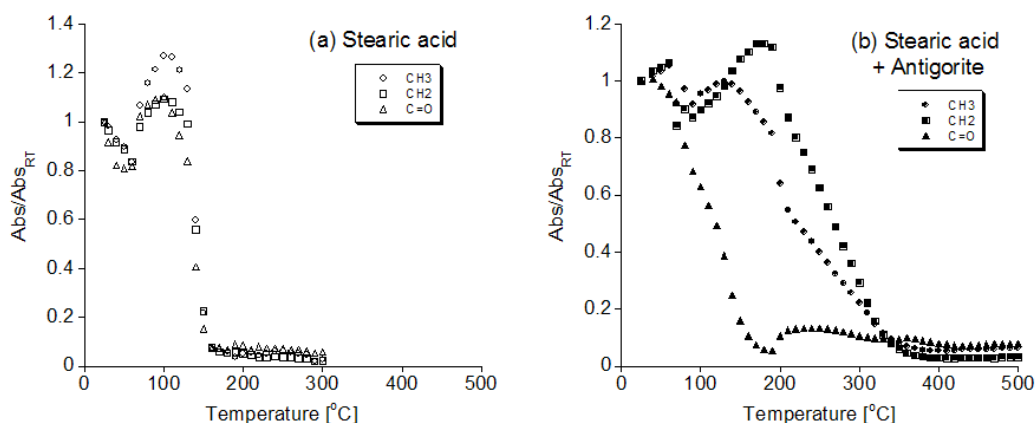


Fig. 7. Changes with temperature of the peak heights for aliphatic C–H and C=O. (a) stearic acid: aliphatic C–H 2955-2954 cm^{-1} and 2927-2917 cm^{-1} peaks with 3000-2800 cm^{-1} baseline and C=O 1715-1700 cm^{-1} peaks with 1830-1370 cm^{-1} baseline. (b) stearic acid with antigorite: aliphatic C–H 2954 cm^{-1} and 2933-2919 cm^{-1} peaks with 3120-2770 cm^{-1} baseline and C=O 1714-1700 cm^{-1} peaks with 1900-1500 cm^{-1} baseline. The peak heights (absorbance: Abs) are normalized to their values at room temperature (Abs_{RT}).

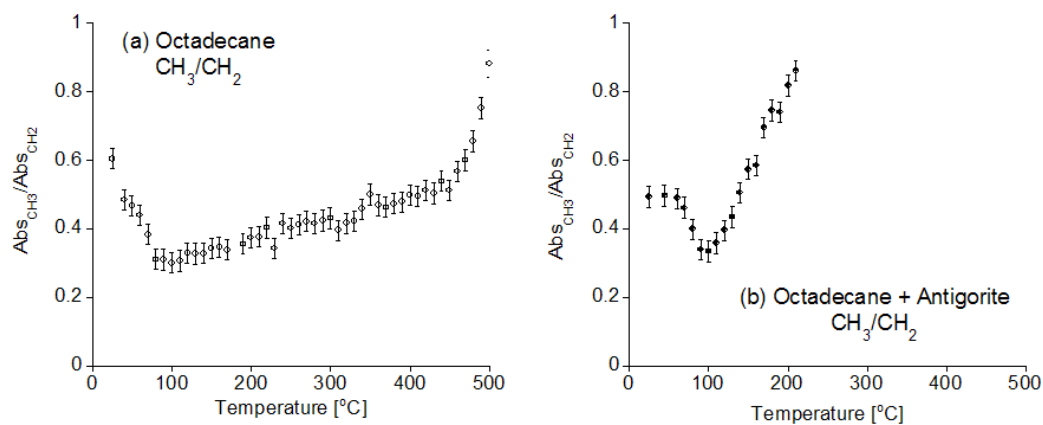


Fig. 8. Changes with temperature of the peak height ratio CH_3/CH_2 for aliphatic C–H.
(a) octadecane; (b) octadecane with antigorite.

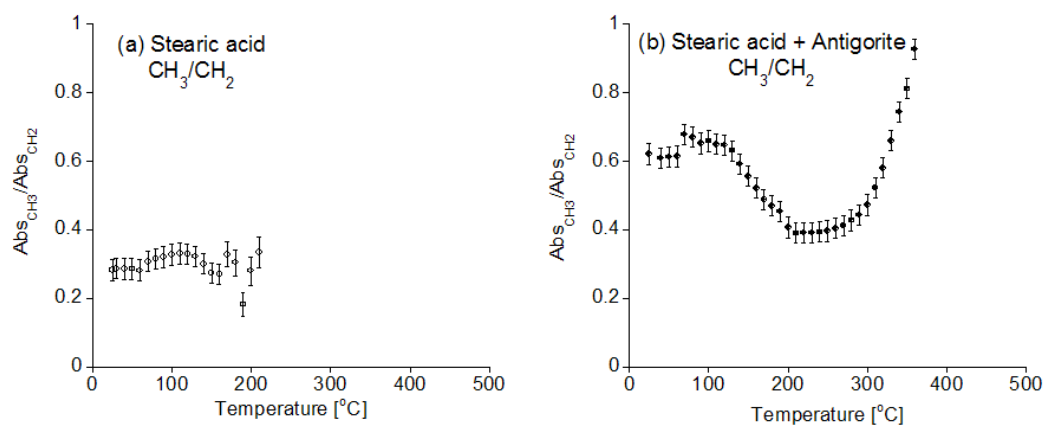


Fig. 9. Changes with temperature of the peak height ratio CH_3/CH_2 for aliphatic C–H
of (a) stearic acid; (b) stearic acid with antigorite.